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Enhancement of Cassava Rhizome Gasification Using Mono - Metallic Cobalt Catalysts

Panchaluck Sornkade[a], Duangduen Atong[a] and Viboon Sricharoenchaikul[b,*]

[a]*National Metal and Materials Technology Center, Thailand Science Park, Pathumthani 12120, Thailand*
[b]*Department of Environmental Engineering, Faculty of Engineering,Chulalongkorn University, Bangkok 10330, Thailand*

Abstract

This paper proposed cobalt catalysts for the in-situ catalytic gasification of cassava rhizome which represented an important stage in the production of hydrogen-rich gas that suitable for internal combustion and direct-fired industrial gas turbine. The study focused on the comparison of syngas (synthesis gas) production from non-catalytic air-gasification of the cassava rhizome at temperatures from 873 – 1073 K, the equivalence ratio (ER) of 0.2-0.4, and continuously feed rate of 30 minutes to the catalytic gasification where the cassava rhizome was mixed with 12Co/α-Al_2O_3 catalyst. The gas yields, hydrogen-carbon conversions and lower heating value (LHV) were compared. The yields of gas products, char and tar for non-catalytic case were 76%, 8.6% and 15%, respectively. Addition of 12Co/α-Al_2O_3 catalyst improved the gas product yields to 81% while char and tar were reduced to 10% and 8.5%, respectively. With 12Co/α-Al_2O_3 catalyst, the highest hydrogen and carbon conversions to H_2 and CO were 4% and 15% more than non-catalytic runs. The lower heating value (LHV) of producer gas was 8.11 MJ/m^3 compared to the non-catalytic case LHV of only 4.12 MJ/m^3. The results indicated that 12Co/α-Al_2O_3 catalyst with reaction temperature of 1073 K and ER of 0.4 yielded high tar reducing performance during air-gasification of the cassava rhizome.

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Keywords: Cassava rhizome; Cobalt Catalyst; Gasification ;

1. Introduction

Biomass can be thermally converted in gasification process to generate various products which mainly consist of gas, tar, char as well as some potentially harmful substances. Several agricultural residues such as pine sawdust, oak sawdust, and birch were studied and gasified by researchers [1-4]. One of the main

* Corresponding author. Tel.: +66-2218-6689; Fax: +66-2218-6666.
E-mail address: viboon.sr@chula.ac.th.

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problems in biomass gasification is tar, particulate and other poisoning substances. Most of them remain in the unit process that can block the filters and other parts in the gasification system. To alleviate these problems in biomass gasification, syngas can be cleaned and tar can be reduced by means of adjusting operating conditions, using mechanical separations (cyclones, filters and scrubbers) and implementing catalytic gasification treatment. The use of catalytic processes can be separated into 2 methods: primary (in-situ) and secondary. In primary method, catalysts are added directly to biomass prior to feeding into the gasifier while the later method involves addition of catalysts in a secondary reactor. Catalysts can be operated under condition in gasification system. The advantage of catalytic system for tar conversion is its sound economic and technical feasibility for gas cleaning. It has the potential to increase conversion efficiencies and ease collection and disposal of tars. The catalytic conversion of tars is commonly known as hot gas cleaning. Several biomass have been tested various types of catalysts such as minerals (dolomite, olivine, limonite, and iron ores) or metal-based (rubidium, cesium, and nickel) in biomass gasification [5-7]. These catalysts were found to be highly effective for tar reduction and char formation from gasification process. Cobalt catalysts were reported as effective catalysts for the steam gasification of wood and biomass. Co-supported on MgO catalysts were investigated for steam reforming of naphthalene as tar model compound in some studies [8]. However, there are no reports about using cobalt-based catalysts with cassava rhizome gasification.

The aim of this work is to study the quality of synthesis gas produced from gasification using different operating conditions (ER and temperature) using an updraft fixed bed gasifier with primary catalytic method of cobalt supported on α-Al_2O_3 catalyst.

2. Experimental

2.1. Biomass preparation and characterization

The cassava rhizome (CR) sample selected for this work was obtained from tapioca fields in Rayong province, Thailand. CR sample was dried to reduce moisture content to less than 10 wt%., and was grinded to about 0.2–1.0 mm size (Fig. 1). Analysis results of the sample are listed in Table 1. CR was mixed with 20 wt% catalyst prior to feeding into the gasification reactor.

Fig. 1. The cassava rhizome before and after grinding

Table 1. Characteristics of cassava rhizome

Proximate analysis	wt.% (dry)	Ultimate analysis	wt.% (dry)
Moisture	8.60	C	37.60
Ash	0.74	H	5.41
Volatile matter	74.70	N	0.37
Fixed carbon	15.96	S	0.69
LHV (MJ/kg)	15.37		

2.2. Catalyst preparation and characterization

In this experiment, α-Al_2O_3 supporter has surface area of 7.39 m^2/g. 12Co/α-Al_2O_3 catalyst was synthesized by impregnation method. In a typical preparation, catalyst was calcined in air at 1123 K for 3 h and reduced in H_2 at 973 K for 2 h and sieved to particle size of 15 μm.

The specific surface area of catalyst determined by the BET method is 1.20 m^2/g. SEM analysis of catalyst is illustrated in Fig. 2a. Energy Dispersive X-ray (EDX) analysis was carried out to determine the chemical composition of 12Co/α-Al_2O_3 and the 12% of cobalt were confirmed in Fig. 2b. The phase of fresh catalyst was identified by using the XRD analysis under air atmosphere at 30 keV, 40 mA, wave length 1.54056 Å Cu/K-α1 radiations, and Bragg-Brentano 2θ configuration. The major peak intensity of active Co phase was located at 44.16º.

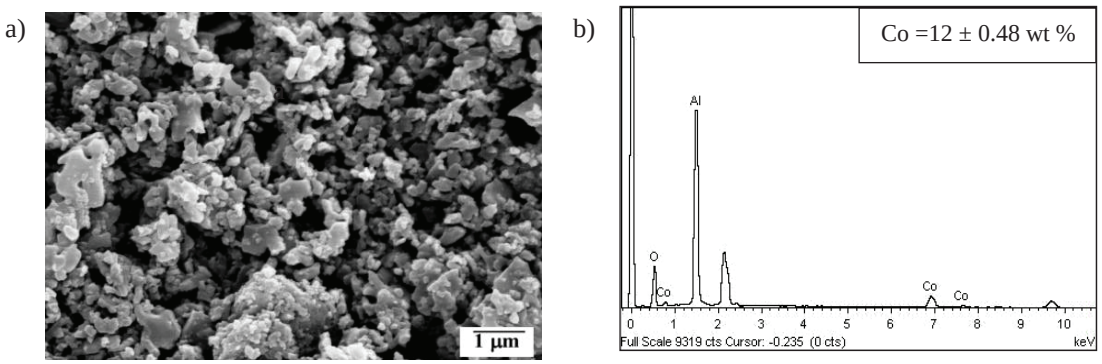

Fig. 2. (a) SEM image of 12Co/α-Al_2O_3; (b) EDX analysis

2.3. Gasification setup

Gasification system consisted of feeder, electrical furnace and reactor (stainless steel updraft fixed bed gasifier). The gasifier has an inner diameter of 1.85 cm and height of 110 cm. The bed medium of alumina balls with 0.1 cm particle diameter were situated at the bottom of the reactor. Reaction temperature was regulated by PID temperature controller from 873 – 1073 K. The carrier gas (nitrogen) was warm up by pre-heater prior to entering the reaction zone. Additional oxygen was mixed with nitrogen to achieve equivalence ratio (ER) of 0.2 - 0.4. Theoretically, ER is one of the most important

operational variables in biomass gasification with the air. It is defined as the oxygen-to-fuel weight ratio divided by the stoichiometric oxygen-to-fuel ratio.

The sample was continuously fed into the system at a rate of 3.0 g/min for 30 minutes. The gas products passed through cyclone to collect any char and ash particles. The liquid products such as tar and other heavy hydrocarbons and water are retained in a system of four condensers and gas-cleaning units. Finally, clean gas products were analyzed by online gas analyzer (MRU GmbH, SWG200^{-1}) which the capable of continuous real time quantification of CO_2, CO, H_2, and CH_4. The diagram of gasification system was presented in Fig. 3.

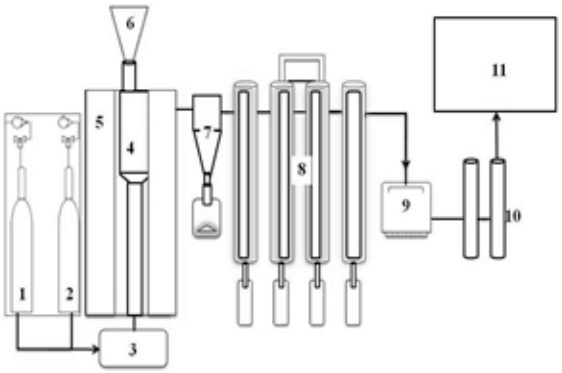

Fig. 3. Schematic of gasification system: (1) - (2) carrier gases (3) gas pre-heater (4) fixed bed reactor (5) electric furnace (6) feeder (7) cyclone (8) condensers (9) gas flow meter (10) gas washer (11) gas analyzer

3. Results and discussion

Typically, biomass gasification is carried out in the temperature range of 873 – 1173 K [9]. Biomass gasification rate is generally too low when the temperature is below 873 K. Many plausible reactions involving various C-containing components of biomass during gasification were described by the equations below:

$$C + O_2 \longrightarrow CO_2 \quad (1)$$

$$C + CO_2 \longrightarrow 2CO \quad (2)$$

$$C + H_2O \longrightarrow CO + H_2 \quad (3)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (4)$$

$$C + 2H_2 \longrightarrow CH_4 \quad (5)$$

3.1. Influence of ER and temperature on CR gasification

Two gasification operating parameters were varied in order to study their effects on syngas, char, tar formation, and the heating value which were ER (0.2 to 0.4) and temperature (873 to 1073 K). Generally, tar and char yields decreased while syngas formation improved when reaction temperature was higher than 873 K. The product distributions from CR gasification under different ER and temperature were

shown in Fig. 4. By gravimetric method of product yields, the minimum tar and char contents of 15.0% and 7.2%, respectively, were obtained at ER of 0.4 at temperature of 973 K. Increasing temperature from 873 - 1073 K and ER from 0.2 - 0.4, gas product roughly improved on average of about 14.5% while tar and char decreased by 5.0 and 9.6%, respectively. It can be noted that higher temperature permitted greater water gas shift reaction of hydrocarbon which assist the decomposition of cellulose and volatile matter in cassava rhizome into gaseous phase. At the same time, cassava rhizome also decomposed to tar, char and other small particles.

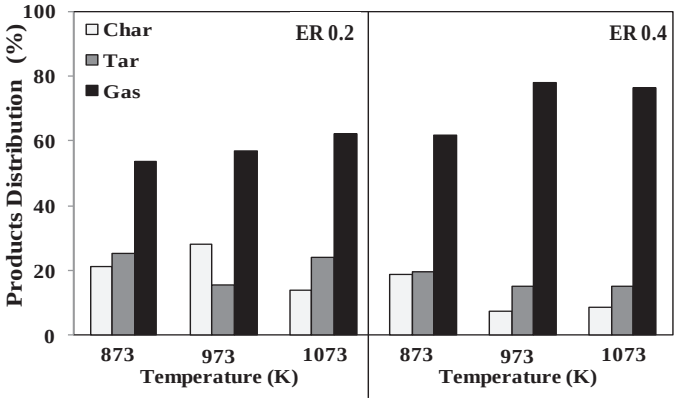

Fig.4. Products from cassava rhizome gasification.

The gas composition (CO_2, CO, H_2, and CH_4) during gasification at different ER was listed in Table 2. In term of gas yields, higher ER promoted the oxidization reactions. It can be observed that at ER 0.2, H_2 content is more than that of ER 0.4.

Table 2. Product Gas with Catalysts Compared with Non-Catalytic case at 1073 K.

Gas content	Gas (vol %)		
	Non-catalytic case		catalytic case
	ER 0.2	ER 0.4	ER 0.4
CO	5.84	8.41	14.84
H_2	7.79	3.07	4.61
CH_4	4.03	7.62	16.06
CO_2	11.09	14.70	19.57

The LHVs of product gas increase due to higher yields of CO and some permanent gas species (hydrocarbons gaseous). In this case, LHVs of the gas yield were calculated by Equation (6).

$$LHV = (0.126\times CO)+(0.108\times H2)+(0.358\times CH4) \quad (6)$$

CO, H_2, and CH_4 are volume (molar) percentage of these gas species, respectively. As seen in Fig. 5, the total gas outlet velocity and LHV of gas products also directly varied with ER and temperature. The

high contents of volatile matter and other organic components (C and H) of cassava rhizome led to high LHV with a maximum value of 4.12 MJ/m^3 at 1073 K.

The result was similar to LHV data from previous works [10-11], air gasification of biomass at temperature of 1173 and 1373 K resulted in product gas with LHV of 4-6 MJ/m^3.

Thermal efficiency or cold gas efficiency (CGE) is defined as energy content in the gas to energy content in the biomass fed. It is calculated from Equation (7).

$$CGE = (V_g \times LHV_g / Mb_m \times LHV_{bm}) \times 100 \quad (7)$$

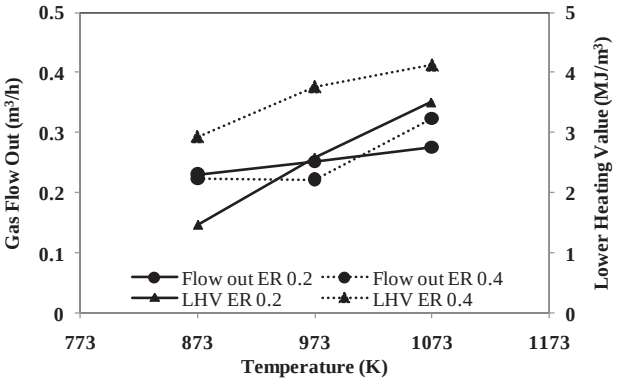

Fig. 5. Gas Flow Out in Exit Gas and LHV in Gas Products

V_g is gas volume flow rate (m^3/h), LHV_g is heating value of gas yield (MJ/m^3), M_{bm} is rate of biomass sample feed to the gasifier (kg/h), and LHV_{bm} is heating value of biomass (MJ/m^3). As listed in Table 3, the CGE is directly depended on the rate of the combustible gas evolved from gasifier. It can be found that ranges of CGE varied with ER of 0.2 and 0.4 between 14-39% and 27-54%, respectively. In addition, higher temperatures led to higher CGE. The result was similar to biomass air-blown gasification case [3], the maximum CGE was 50-60%. Comparing to previous work [12] which utilized H_2O/O_2 as gasifying agent, this work employed air which tended to yield lower efficiency than N_2-free H_2O/O_2 gasification product. Moreover, CO and H_2 from H_2O/O_2 fed also affected H_2O/O_2 ratio. Higher H_2O/O_2 ratio gave higher gas yield and CGE.

Table 3. CGE of Cassava Rhizome Gasification in Non-Catalytic Case

Temperature (K)	Cold Gas Efficiency (%)	
	ER 0.2	ER 0.4
873	13.68	26.36
973	26.19	33.56
1073	38.43	53.97

3.2. Influence of 12Co/α-Al2O3 catalyst

The reaction at 1073 K and ER 0.4 were selected for catalytic study. Co/α-Al_2O_3 catalyst significantly improved gas production as compared with non-catalytic gasification. Co/α-Al_2O_3 was also effective on heavy tar cracking. Tar was reduced greatly for 57.2% and converted to gas. It might be that tar reaction was more reactive than char when air was used as gasifying agent. Similarly with Tasaka et al. [13], performance of 12Co/MgO catalyst was outstanding for tar reducing in steam gasification of radiata pine.
In term of gas species, Co/α-Al_2O_3 seemed to promoted boudouard reaction (Equation 2) and methanation reaction (Equation 5) as CO and CH_4 were presented in large amount (Table 2).
As illustrated in Fig. 6, in case of Co/α-Al_2O_3, C and H conversion to CO and H_2 reached about 36.80 and 13.30 %, respectively. Meanwhile without Co/α-Al_2O_3, C and H conversion were 22.11 and 9.40%, respectively. LHV of gas products with Co/α-Al_2O_3 catalyst was 8.11 MJ/m^3 which was significantly greater than LHV from non-catalytic case (4.12 MJ/m^3).

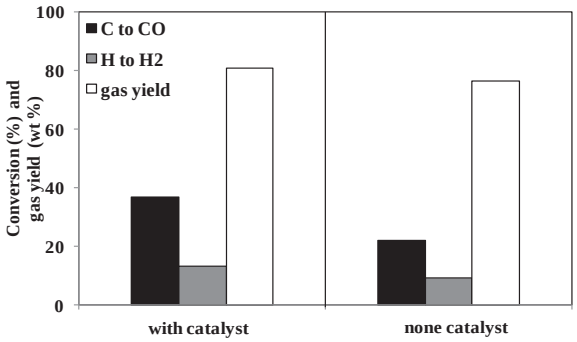

Fig.6. The Conversion of Carbon and Hydrogen.

The XRD measurement was performed to determine the composition of spent Co/α-Al_2O_3 after one round of in-situ gasification, as illustrated in Fig. 7. Phase of metallic cobalt (Co^0) was identified at 2θ of 44.16° for fresh catalyst. After gasified, XRD detected the CoO_2 phases at 20.95°. Co^0 phase disappeared after reduction because the redox reaction slightly occurred over catalyst surface and the thermal decomposition.

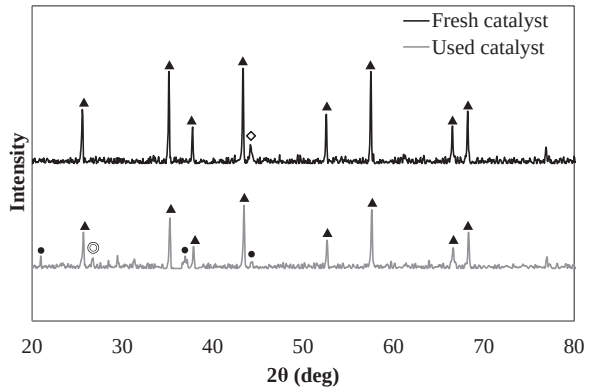

Fig. 7. XRD analysis of Co/α -Al_2O_3 catalyst (◇Co, ▲Al_2O_3, • CoO_2, ◎ Carbon)

The gas outlet velocity of catalytic gasification was 0.31 m^3/h which was very closed to non-catalytic case (0.32 m^3/h). It seemed that flow rate of gas products was independent on whether catalyst was being used or not. In case of Co/α-Al_2O_3 catalyst, the maximum CGE was improved to 96.40% while only 53.79% was obtained in non-catalytic case. Obviously, LHV of gas products of 8.11 MJ/m^3 for catalytic runs indicted improvement of CO, H_2 and CH_4 production when compared with non-catalytic case.

4. Conclusion

In the updraft fixed bed air gasification of cassava rhizome, the temperature and ER are important factors to the performance of the process. Higher temperature was more favorable in term of total products, LHV, and gas outlet quantity. The temperature of 1073 K with ER of 0.4 was the optimum condition to obtain product gas with acceptable quality. Meanwhile, additional of Co/α-Al_2O_3 catalyst help reduce tar formation and greatly improved gas yield, gas composition, LHV, system efficiency, and C-H conversion to syngas.

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